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Characterization of Nanostructured TiZrN Thin Films Deposited by Reactive DC Magnetron Co-sputtering

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Abstract

The ternary nitride TiZrN thin films were deposited by reactive DC Magnetron co-sputtering technique with different titanium sputtering current (I_{Ti}) ranging from 0.6 to 1.2 A, using individual Ti and Zr co-sputtered targets at constant deposition time. The Ar to N₂ flow rate ratio was fixed at 8:6 sccm. The crystal structure, surface morphology microstructure and element compositions were investigated by X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FE-SEM). It was found that the crystal structure, surface morphology, microstructure and element compositions of the films are strongly dependent on the deposition parameters. All the films are composed of TiZrN crystal structure (111) (200) and (220) planes with preferred orientation of (200) plane. The crystallinity of the films changed as a function of Ti sputtering currents. The AFM measurement indicated that the coarse and congregate grain with increasing of I_{Ti} were not only enhanced root mean square roughness (R_{rms}) from 2.7 to 11.6 nm, but also increases average thickness continuously from 347.1 nm to 751.8 nm. With the increase of I_{Ti} the atomic ratio of Ti to Zr elements and the N to (Ti + Zr) ratio increased to 0.9 and 1.6, respectively.

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Keywords: Titanium Sputtering Current; TiZrN; Reactive DC Magnetron Co-sputtering

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1. Introduction

The 4th group transition metal nitride TiN has been provide to commercial application for cutting and machining tools in the industry [1,2] due to their superior characteristics such as high hardness, high thermal and chemical stability, low electrical resistivity, good wear resistance and better mechanical [3]. However, the limited of TiN are that they are not stable by occurring oxidation resistance at high temperatures beyond 500^oC that can be reached during machining processes [4-6]. In practice, it has been reported that the effect of adding zirconium in to TiN structure to form TiZrN films not only have superior wear resistance due to formation of the stable oxide layers on the film but also increased hardness by solid solution strengthening [7].

There are different techniques and methods to deposit TiZrN thin films, such as DC or RF reactive sputtering [8, 9] and vacuum arc deposition [10]. Most of them were prepared at high arc current [10, 11] applied bias voltage [1, 12], and substrate heating [1, 9, 13] to obtained TiZrN nanostructure. However, the advantage of sputtering technique are low temperature with no additional heating process to substrates and no bias substrate can shorten the production time and consequently reduce production costs.

The aim of this study was to deposit nanostructured TiZrN thin films on unheated substrates without substrate biasing at different Ti sputtering currents by a DC reactive unbalanced magnetron Co-sputtering system. The Influences of Ti sputtering currents on the crystal structure, surface morphology, microstructure and elements compositions were investigated.

2. Experimental

The nanocomposite TiZrN films were deposited on silicon wafer (100) and glass slide substrates at room temperature by a reactive DC magnetron co-sputtering as show in Fig.1 from titanium (Ti) and zirconium (Zr) targets of high purity 99.97% and 99.95%, respectively. The base pressure was reduced to 5.0×10^{-5} mbar then the targets were pre-sputtered for 5 min in order to eliminate the contaminant from target surfaces, followed by injected high purity (99.999%) nitrogen reactive gas into the vacuum chamber to form titanium zirconium nitride thin films. The argon and nitrogen flow rate were fixed at constant value for all coating. The deposition parameters for TiZrN coating were listed in table 1.

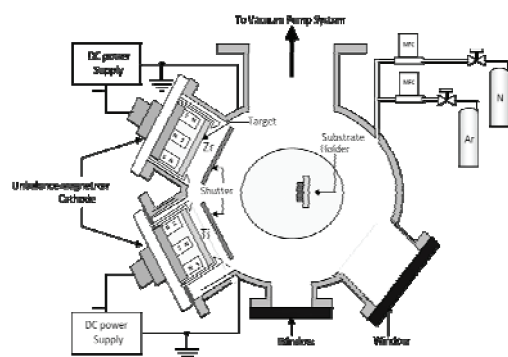


Table 1. Deposition conditions of TiZrN thin film

Parameters	Values
Base pressure (mbar)	5.0×10^{-5}
Deposition pressure (mbar)	5.0×10^{-3}
Substrates	Si (100) and glass slide
Ar : N ₂ flow rate (sccm)	8 : 6
Ti sputtering current (A)	0.6, 0.8, 1.0, 1.2
Zr sputtering current (A)	0.6
Deposition time (min)	60
Target to substrate distance (cm)	13

Fig. 1. Schematic representation of the reactor

The crystal structure and phase development of the films were analyzed by x-ray diffractometer (XRD) (Rigaku, Rint 2000) using Cu K α radiation operated at 40kV and 40 mA with grazing incidence angle set at 3° and scanning speed of 2°/min. The surface morphology and thickness were evaluated by atomic force microscope (AFM) (Nanoscope IV, Veeco Instrument Inc) using scanning area of 1 x 1 μm^2 . The microstructure was investigated by field emission scanning electron microscope (FE-SEM) and element analysis was carried out employing energy dispersive spectrometry (EDS) together with Hitachi s-4700 equipment.

3. Results and Discussions

3.1. Crystal Structure

From the Fig. 2, the XRD measurements indicated that the films were cubic structure. The patterns showed peaks diffractive angles at 36.46°, 42.36°, 56.50°, 61.92° and 73.70° which correspond to TiZrN (111), TiZrN (200), silicon (100), TiZrN (220) and TiZrN (222) planes, respectively. The small peaks of (111) and (220) planes were appeared on film deposited for 0.6 A. With increase of current, the XRD intensity of (111) plane (220) and (222) plane were increased but decreased for (200) plane. The intensity of (200) plane was significant changed which exhibit prefer orientation with highest intensity. The development of crystal structure was attributed to the addition energy of deposition atoms on substrate surface during film formation which leads to an increase adatom mobility and hence more crystallinity of the films through longer deposition time. Furthermore, the observation that the XRD 2 θ peaks shift toward lower Bragg angles comparing to the standard TiN diffraction pattern, which indicates the extraction of lattice by the substitution of Zr atoms into Ti atoms in the TiN structure. This is clarified by the fact that the covalent radius of zirconium (0.147 nm) is larger than that of titanium (0.146 nm).

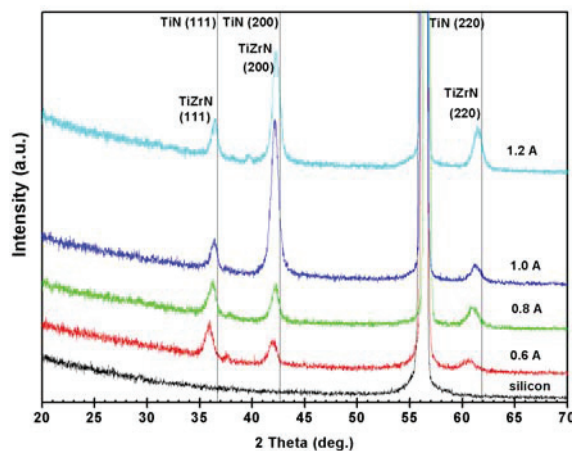


Fig. 2. The XRD pattern of TiZrN thin film deposited at different Ti sputtering currents

3.2 Surface morphologies

The AFM images of surface morphology of coatings are shown in Fig. 3 with display three-dimensional representations (1 $\mu\text{m} \times 1\mu\text{m}$ surface plots), corresponding to the samples prepared at current of 0.6, 0.8, 1.0 and 1.2 A. They are show mainly composed of individual grain with equal size and compact pattern of sample deposited at 0.6 A. All of grains deposited at 0.8 A are tend to bigger, higher

and spread across the surface. For the films deposited at 1.0 A, the grain sizes are gradually increases with more triangle pattern. The grain sizes were coalescent to become the bigger size of triangle shape with more valley pattern and open structure located along the surface which observed at of 1.2 A. The root mean square roughness (rms) values of the samples are 2.7, 4.9, 6.5 and 11.6 nm, respectively. AFM indicate continuous increases in average thickness from 347.08 nm to 751.77 nm by increasing the current. The result related to the enhancement of atom energy and the increasing of titanium current and also affecting thickness of the films by more Ti particles off the target.

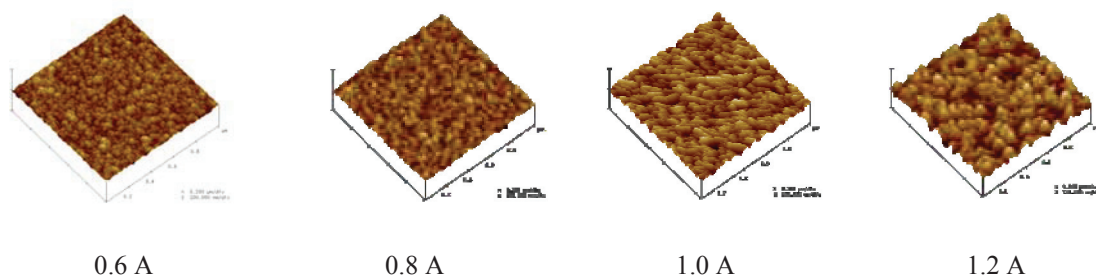


Fig. 3. Surface morphology of TiZrN deposited at different ITi

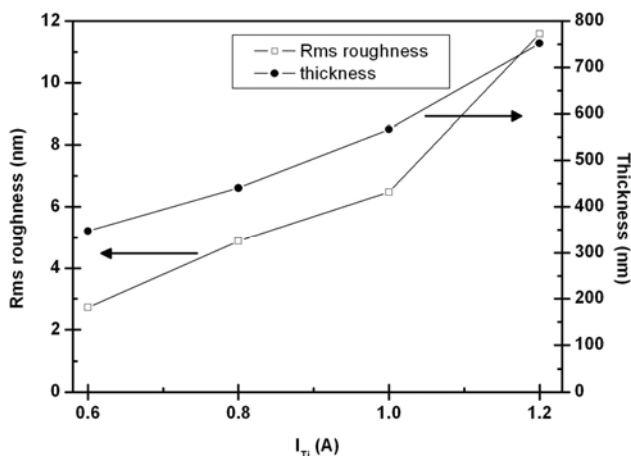


Fig. 4. Rms roughness and thickness as a function of ITi

3.2. Microstructure

FE-SEM images in Fig.5 also show the surface microstructure of as-deposited TiZrN thin films which substantial difference between four sputtering currents. A densified structure with much finer grain size were observed at I_{Ti} of 0.6 A. As the sputtering current increased to 0.8 A, the films show small facet column across the surface and larger facet were shown at 1.0 A. The film deposited at I_{Ti} of 1.2 A exhibited porous tapered columnar structure with highest porosity which corresponds to the zone T structure [14]. In addition, the results showed that changes in the sputtering current only strongly influenced the chemical composition of the coatings, Fig. 6. The nitrogen content was found to rapidly increase from 43.372 at% to 61.60 at% with increasing titanium sputtering current. On the other hand, the titanium content increased slightly from 14.390 at% to 18.125 at% and the zirconium content decreased

significantly from 41.768 at% to 20.026 at%, the atomic ratio of Ti to Zr elements and the N to (Ti + Zr) ratio increased to 0.9 and 1.6, respectively.

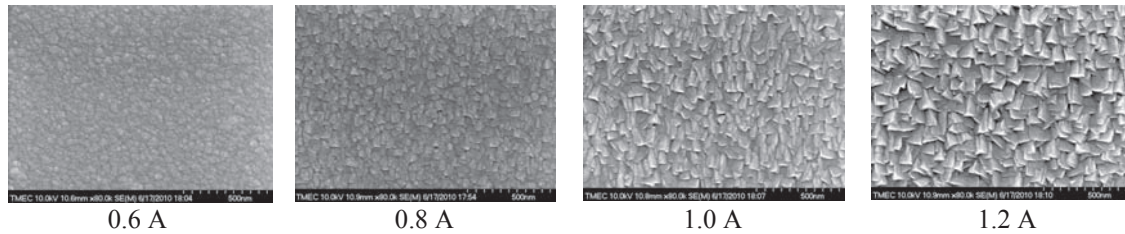


Fig. 5. FE-SEM micrographs of TiZrN thin film deposited at different I_{Ti}

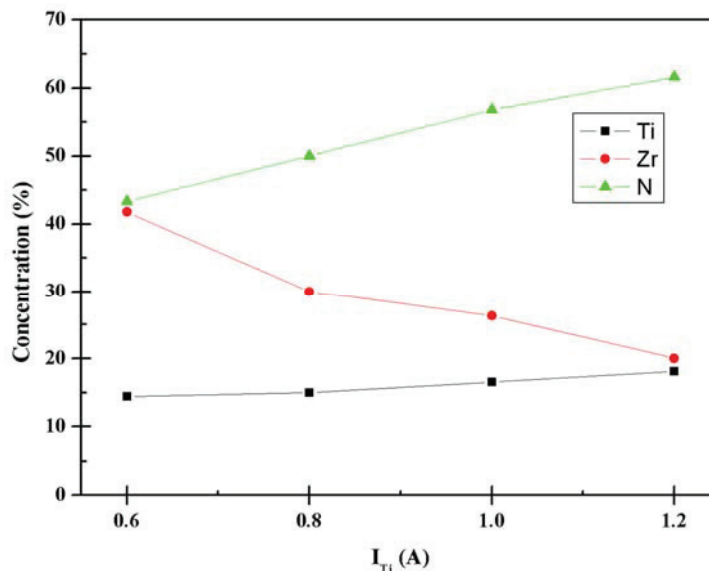


Fig. 6. Element concentration (%) of TiZrN coating as a function of I_{Ti}

4. Conclusions

Nanocrystalline titanium zirconium nitride (TiZrN) thin films were successfully deposited on unheated substrate without biasing by reactive DC magnetron co-sputtering technique. The crystal structure, the surface morphology, microstructure and elements compositions strongly influenced by Ti sputtering current. The TiZrN (111), (200) and (220) planes which shift backward to lower 2θ were obtained by XRD. With the increase of titanium sputtering current, the crystallinity of (200) plane was significant altered with respect to other planes. It was found the not only the coalescent of the grain along the surface but also surface roughness and the average thicknesses of the films were increased for higher sputtering current with in the range of 2.7 to 11.6 nm and 347.1 to 751.8 nm, respectively. The microstructure changed from densified structure to columnar with high porosity pattern observed by FE-SEM technique. Further investigation concerning the elements composition using EDS analysis showed a variation of Ti,

Zr and N compositions which between 14.390 - 18.125 at%, 41.768 - 20.026 at% and 43.372 at% to 61.600 at%, through the Ti sputtering current.

Acknowledgements

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